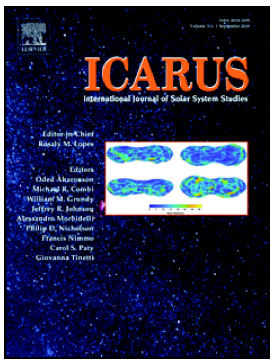

Effects of UV-organic interaction and Martian conditions on the survivability of organics

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Effects of UV-organic interaction and Martian conditions on the survivability of organics

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Running title: Effects of UV-organic interactions

Abstract

Exogenous organic molecules are delivered to the surface of Mars annually, yet their fate is largely unknown. Likewise, the survivability of putative organic biomarkers directly implicates current Mars surface exploration ambitions. Among these, amino acids are valuable target molecules due to their abiogenic and biological origins. We present the fundamental, but not previously considered, factors that affect the fate of amino acids embedded in Mars mineral analogues when exposed to ionising radiation. Using existing experimental datasets, we show that the attenuation coefficient at 200 nm for amino acids is an effective parameter for quantifying organic survivability, especially when mineral shielding is limited or absent. Conversely, the dielectric constant of a material is a potential keyparameter regarding mineral shielding, as it accounts for iron content, and

the physical properties of the material (pore size, surface area or water content). Finally, we combine Martian climatic parameters (surface temperature and atmospheric opacity) to show that the relative UV environment varies significantly on Mars as a function of latitude, providing a reference point for future Mars simulation studies.

Keywords: irradiation; Mars; analogue; attenuation coefficient; amino acids.

1. Introduction

Exogenous delivery of organic matter is a daily process on Mars via meteorites, interplanetary dust particles (IDPs) and micrometeorites (up to 4×10^{-4} g. $m^{-2}yr^{-1}$; Flynn and McKay, 1990), with thiophenic, aromatic, and aliphatic complex compounds recently identified at Gale crater (Eigenbrode et al. 2018), along with seasonal methane (Webster et al. 2018). However, the challenge in detecting organic molecules in Martian surface materials remains a significant obstacle in assessing Martian habitability and the future detection of organic biosignatures.

Among the family of organics of astrobiological interest, amino acids are valuable targets (Parnell et al, 2007). Present in comets and meteorites (Elsila et al. 2009; Martins and Sephton 2009; Altwegg et al. 2016), they can be produced in cold, ionised, astrophysical environments (Bernstein et al. 2001; Ehrenfreund et al. 2001; Caro et al. 2002; Meinert et al. 2012; Modica et al. 2014; 2018), and through cometary impacts (Martins et al. 2013). Amino acids are sensitive to ionising radiation, and experimental studies have shown they have limited stability against UV photo-destruction when embedded in materials that are easily penetrated by UV photons (Ehrenfreund & Chanrley, 2000). Once on planetary environment, the amino acid preservability results from the actions of competing catalytic effects, mitigated by the host mineral properties (see Fornaro et al. 2018b). As such, survivability of amino acids within the near-surface Martian crust is a key issue for current (NASA Mars Science Laboratory) and

future (NASA Mars2020; Williford et al. 2018, and ESA ExoMars 2020; Vago et al., 2017) surface missions.

Low-Earth orbit exposure experiments have shown a higher sensitivity of amino acids compared to peptide, and the limited shielding by montmorillonite clay (AMINO experiment, Boillot et al. 2002). The role of the ionising wavelength and the amino acid chemical structure in their photo-degradation has also been previously investigated (Bertrand et al, 2015). Experiments under simulated Martian conditions have shown that factors including low temperature (210 K, ten Kate et al. 2006) and a clay-mineral host (Poch et al, 2015) have a protective effect on amino acids, and dos Santos et al (2016) investigated the survivability of amino acids embedded in Mars mineral analogues under simulated Martian surface conditions.. This study shows that the high surface area and small pore sizes of clay minerals, and the high UV-opacity of sulfates and olivine, limit the photo-destruction of adsorbed amino acids. Here we argue that in addition to these mineralogical effects, there are fundamental physical effects imparted by the interaction of ionising radiation with amino acid molecules that need to be considered, particularly where laboratory simulation of the whole ionising spectrum (photons, protons, electrons) reaching the surface of Mars is limited. This has implications for future studies that seek to address a causal relationship between geological properties and biomarker preservation. We use the attenuation coefficient of amino acids as a tool to discriminate the role of mineralogy in the preservation of amino acids under simulated Martian conditions. The attenuation coefficient (expressed as molar or mass attenuation coefficient) refers to the propensity of matter to interact with, and absorb, incoming radiation. In this case, this is the propensity of molecules to become electronically excited under UV radiation, resulting in changes to the structure of the molecule (mass loss, bonds breaking, and structural rearrangement). The attenuation coefficient is primarily related to the molecular structure of a compound, even though environmental parameters such as temperature and pressure are also

important. In addition, UV photons are a major feature of the Martian surface (as well as most planetary environments), but UV photolysis intrinsically differs from radiolysis induced by charged particles, and requires a different calculation (DeWitt et al. 1993).

2. Methods

2.1 Determination of the absorbed energy as a function of photon wavelength

Mid- and far-UV wavelengths have enough energy to destabilize the electronic structure within solids and break most simple carbon bonds (see Sanderson 1976). Due to the dual nature wavelength-particle of UV-photons and their inability to destabilize inner-shell electrons within solids (like electrons or protons, Nikjoo et al. 2012), they should be treated separately from other ionising particles present on Mars surface. Photons have a much lower probability of interaction with matter than charged particles, and there is no stopping power (i.e. the direct energy transfer rate within the solid) for photons (Andreo and Brahme 1986). In this case, the stopping power can be inferred by the probability of an interaction of the solid, called the attenuation coefficient.

Identical fluencies can result in different absorbed energy, with various structural damages, because the energy transfer between a particle and a solid is a direct function of the particle kinetic energy. For electrons, the deposited energy (hereafter called dose) depends on the fluence and the electronic stopping power (the linear rate of the energy transfer between the incoming particle and the target):

$$E = \sigma_E \times F \qquad \text{(Eq.1)}$$

where E is the dose, σ_E is the electronic stopping power and F is the fluence.

To understand the energy deposition by photons (E_γ) and its relationship to the photon energy (i.e. wavelength), we have used the attenuation coefficient ε. The attenuation refers here to the ability, or propensity of a photon to interact with a solid, at a precise wavelength. Thus, this can be used as the probability of the photon-solid interaction, with:

$$E_\gamma = \varepsilon \times E \qquad \text{(Eq. 2)}$$

with E_γ the dose (in $eV.M^{-1}.cm^{-1}$), and E the incident photon energy.

Based on this, we calculate the UV photon energy deposition in different amino acids and complex organic compounds. Organic functional groups comprise carboxylic acid (oxalic acid), aldehyde (butaldehyde), pyridine acid (niacin) and ketone (hydroquinone). These belong to classes previously measured in the Murchison meteorite (Pizzarello and Shock 2010), an organic-rich primitive carbonaceous chondrite. Despite their structural differences, the maximum energy deposition is close to 200 nm (Figure 1). From a purely energetic perspective, at 200 nm photons have enough energy to damage or break most simple C-X bonds in organic or silicate solids (where X is C,H,O,N, Cl or Si, Sanderson 1976). Hence, the attenuation coefficient at 200 nm can be used as a tool to discriminate the extent of damage undergone by amino acid or organics exposed to UV irradiation.

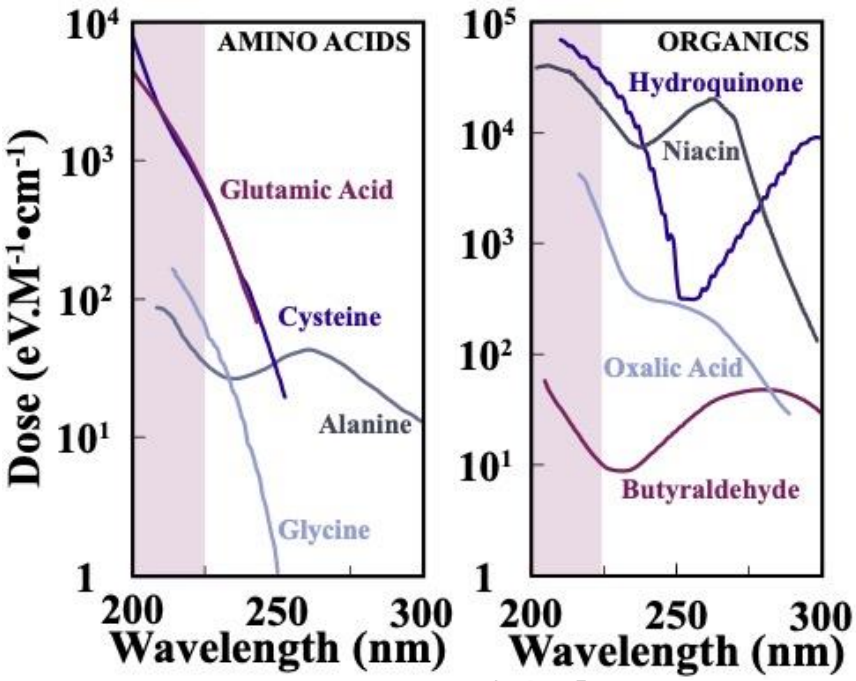

Figure 1. Evolution of the absorbed energy in amino acids (left) and different classes of organics measured in carbonaceous chondrites (right), as a function of photon wavelength (data from NIST UV-vis Reference Database). The purple band shows the wavelengths (between 200 and 225 nm) where the energy deposition is maximum.

2.2. Determination of attenuation coefficients for amino acids.

We selected the available molar attenuation coefficients in the UV wavelength range (data from Goldfarb et al. 1951; table 1) covering 11 of the 25 amino acids investigated by dos Santos et al. (2016). The coefficient values are taken at 205 nm, a spectral region of the highest absorption of most carbon-carbon and carbon-oxygen moieties (De Gruijil, 2000). These coefficients are plotted against the survivability ratio A/A_0 (%) published by dos Santos et al. (2016), where A is the abundance of each amino acid that was not degraded after the simulated Mars chamber experiment, and A_0 is the total abundance of amino acid present in the correspondent control sample (Figure 2). We only consider here the highest concentration of

amino acids (50 µM) used by dos Santos et al. (2016), so to establish an upper estimate of survivability. We note that the concentration of 50 µM is sufficiently low to make sure the amino acid adsorption onto the minerals is a simple exchange with interlayer cations and not other processes, as showed by Parbhakar et al (2007) and Cuadros et al. (2009), and highlighted by dos Santos et al. (2016).

Amino acid	**Molar attenuation coefficient at 205 nm (M cm^{-1})**	**Mineral**	**Iron Content (Fe_2O_3 wt. %)**	**Dielectric Constant At 1 MHz (F m^{-2})**
D-Alanine	79	Hematite	99.0	25
L-Alanine	79	Goethite	92.3	7.0
D-Valine	97	Jarosite	53.7	3.3
L-Valine	97	Nontronite	43.1	39.5
Glycine	54	Olivine (Forsterite)	18.1	7.3
D-Leucine	104	Basaltic Lava	17.3	7.0
L-Leucine	104	Enstatite	15.8	8.5
L-Aspartic	136	Augite	14.0	8.5
D-Aspartic	136	Montmorillonite	3.1	33.0
L-Glutamic	151	Saponite	0.5	17.3
D-Glutamic	151	Gypsum	0.0	8.3

Table 1. Available molar attenuation coefficients of amino acids at 200 nm (from Goldfarb et al, 1952), total Fe content (represented as Fe_2O_3 wt. %) determined for the minerals used in this study, and corresponding dielectric constants (data from Olhoeft 1979; Stillman and Olhoeft 2008, and Cunje et al. 2018.)

2.3 Geological substrates and determination of their total iron content

Twelve mineral phases / geological subtrates representing the key mineral groups found on Mars (Ehlmann and Edwards, 2014) were used by dos Santos et al. (2016), and 11 are studied here: augite, enstatite, goethite, gypsum, hematite, jarosite, montmorillonite, nontronite, olivine, saponite and basaltic lava. A detailed description of the geological samples (including origin, purity and structure) is available in dos Santos et al. (2016). The iron content of clays and other minerals has been shown to influence their UV-transmission behavior (Hoang-Minh et al, 2010), and act as shield against PAH photodegradation. Therefore, the total Fe contents of the minerals used by dos Santos et al. (2016) was determined by using X-ray fluorescence from a Nikon XL3T GOLDD, equipped with an X-ray generator of 50 kV/200 µA (Table 1). All the analyses were performed at least in three spots of about 3 millimeters in diameter. In addition to the internal calibration, the equipment was also calibrated with standards IRRM-BCR-126A – Lead Crystal Glass, and BAM-S005B – Multi-element Glass for XRF Analysis. The estimated error for major elements (Si and Al) was ≤ 3%, for minor elements (K, Ca and Fe) ≤ 4% and for trace elements ≤ 8%.

2.4 Dielectric constant of geological substrates

The dielectric constant refers to the ability of a solid to transfer and/or store energy when submitted to an electric field (here the field is generated during the irradiation). Indicative values for the dielectric constants are taken from Olhoeft 1979 and extrapolated at 1 MHz from Cunje et al. 2018 for clays (montmorillonite and nontronite). Dielectric data have been collected to our best knowledge and availability, and hence for some samples, they are limited (given in

table 1, at 1M Hz). For montmorillonite, nontronite and jarosite, the only dielectric constant value available is the real part of the dielectric constant (ε'), and does not consider an imaginary and frequency dependant part (ε''), that may affect the constant value. A value for saponite is not reported or known.

3. Results and Discussion

3.1 Effect of attenuation coefficient on organic survivability

We identify three different behaviours of amino acid survivability as a function of mineralogy when attenuation coefficients are accounted for (Figure 2). Where a higher amino acid attenuation coefficient (and therefore energy absorbance) corresponds to increased amino acid degradation, the mineral substrate does not play a photo-protective role. This trend is observed for montmorillonite, jarosite, goethite, basalt lava and saponite, and indicates the amino acid response is driven by the molecular structure of the amino acids themselves, rather than by these mineral hosts. Conversely, an opposite trend (higher amino acid attenuation coefficient corresponding with better amino acid survivability) suggests the mineral host is shielding the amino acids from UV irradiation and subsequent photo-degradation, and this is observed for olivine, nontronite and gypsum. As higher attenuation coefficients mean more interactions between photons and molecules, a positive trend results from a real UV-shielding effect of these minerals. Finally, enstatite, augite and hematite do not show any trend (Figure 2B).

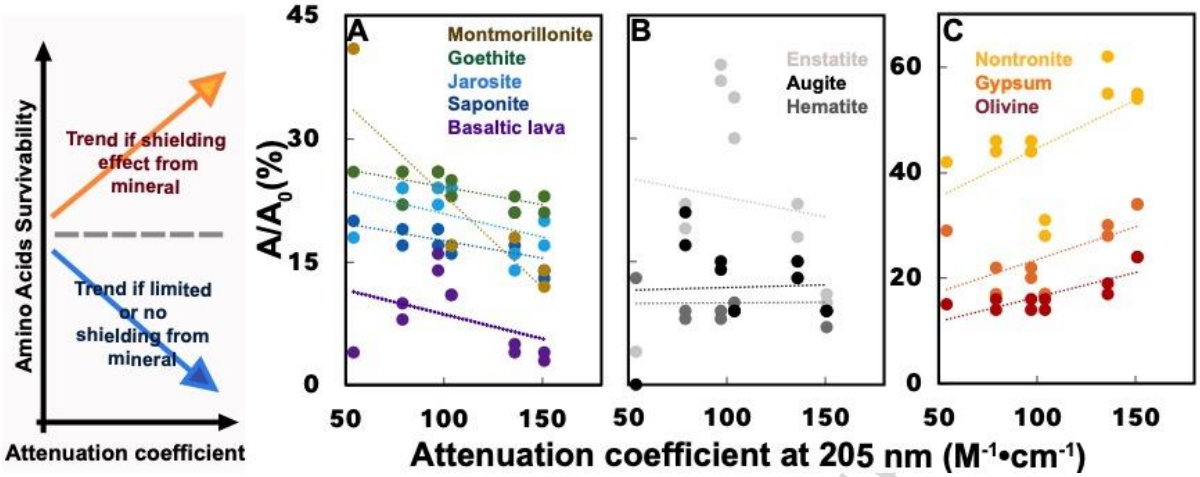

Figure 2. Relative abundance of amino acids preserved after irradiation in Martian-like conditions (A/A_0 %, from dos Santos et al., 2016, and attenuation coefficient from Goldfarb et al. 1951) as a function of the molar attenuation coefficient at 205 nm.

A predicted survivability rate can be derived from the linear correlation between attenuation coefficient and survivability, for samples with absent or limited UV shielding (figure 3-A). Results are given in table 2. These do not include the three larger amino acids with an aromatic ring (tryphtophan, phenylalanine, tyrosine). Aromatic rings are more difficult to destabilize under ionising irradiation, and thus despite a higher molecular weight, a better survivability results from a more complex energy dissipation. From this, all proteins and petides, and one of the amino acids (methionine) are completely destroyed after 6.5 Martian days, while most amino acids survive.

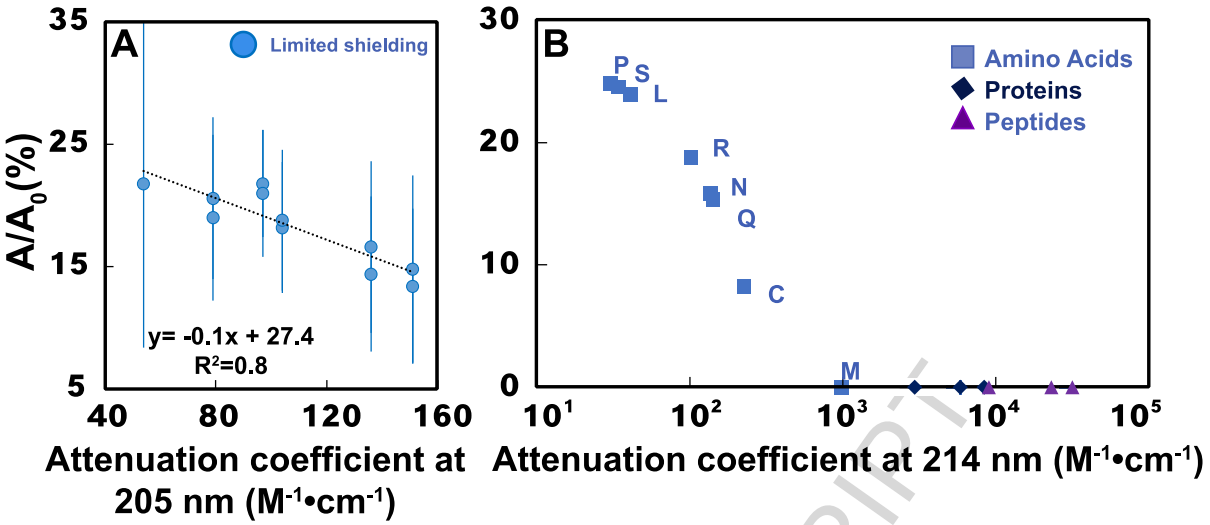

Figure 3. (A) Prediction of the survivability rate (A/A_0) of amino acids as a function of their attenuation coefficient at 205 nm after 6.5 days when the mineral substrate shielding is limited to absent. Values are the average per amino acid, and error bars the standard deviation (1θ) for montmorillonite, jarosite, goethite, lava and saponite. All data come from the 50 µM concentration series (dos Santos et al. 2016), with samples prepared and analysed in the same way. (B) Projection of the survivability rate (A/A_0 %) for amino acids Arginine (R), Lysine (K), Asparagine (N), Methionine (M), Cysteine (C), Proline (P), Glutamine (Q), Serine (S), Threonine (T), proteins (RGDS, GYG, EQLSTSEENSK) and peptides (GPRP, RPPGFSP, RPPGFSPFR) based on their attenuation coefficient at 214 nm (data from Kuipers and Gruppen 2007). Names and data available in Table 2.

Name	Attenuation coefficient at 214 nm ($M\ cm^{-1}$) From Kuipers and Gruppen 2007	Projected Survivability (A/A_0, %) after 6.5 Martian days

Amino Acid		
Arginine (R)	102	19
Lysine (K)	41	24
Asparagine (N)	136	16
Methionine (M)	980	0
Cysteine (C)	225	8
Proline (P)	30	25
Glutamine (Q)	142	15
Serine (S)	34	25
Threonine (T)	41	24
Proteins		
RGDS	2960	0
GYG	5835	0
EQLSTSEENSK	8410	0
Peptides		
GPRP	8980	0
RPPGFSP	23100	0
RPPGFSPFR	31600	0

Table 2. Parameters and projected survivability after 6.5 Martian days for different classes of organics exposed with a limited to absent shielding effect from the mineral surbstrates. Data for the attenuation coefficient are taken from From Kuipers and Gruppen 2007.

Collectively, our results show that the attenuation coefficient as acts as a control for amino acid survivability when the effect of mineral shielding is limited or absent, and can likewise indicate when a mineral host is providing a real shielding effect. This factor can be used for other previous experimental irradiation studies in simulated Martain environments. For example, Kminek and Bada (2006) measured the radiolysis constant for different amino acids, under ionising irradiation (γ-rays), for doses up to 5.42 MGy. They showed a linear dependency of radiolysis constant (related to the extent of structural damages) to amino acid molecular weight (figure 4A). Such linear dependency is also observed when data are plotted as a function of the attenuation coefficient at 205 nm (figure 4B).

It is also possible to determine if mineral substrates are actively shielding embedded

organics subjected to ionising irradiation. Noblet et al. (2012) exposed glycine, serine and mellitic acid, and phthalic acid within Mars regolith simulant JSC Mars-1, to ionising irradiation onboard the International Space Station for 1.5 years. = Their survivability, reported by their relative abundance after irradiation (A/A_0 %), is shown in figure 4C. Preservability for pure serine, glycine and mellitic acid is linearly correlated to the attenuation coefficient at 214 nm (data from Sigma Aldrich), unlike the JSC Mars-1 hosted phtalic acid (figure 4C). These trends are comparable to the results in figure 2, and further suggest that in this example that organic degradation is controlled by their attenuation coefficients. The phthalic acid within the JSC Mars-1 simulant has the highest attenuation coefficient, but shows the highest survivability, suggesting a protective role of the JSC Mars-1 mineral analogue.

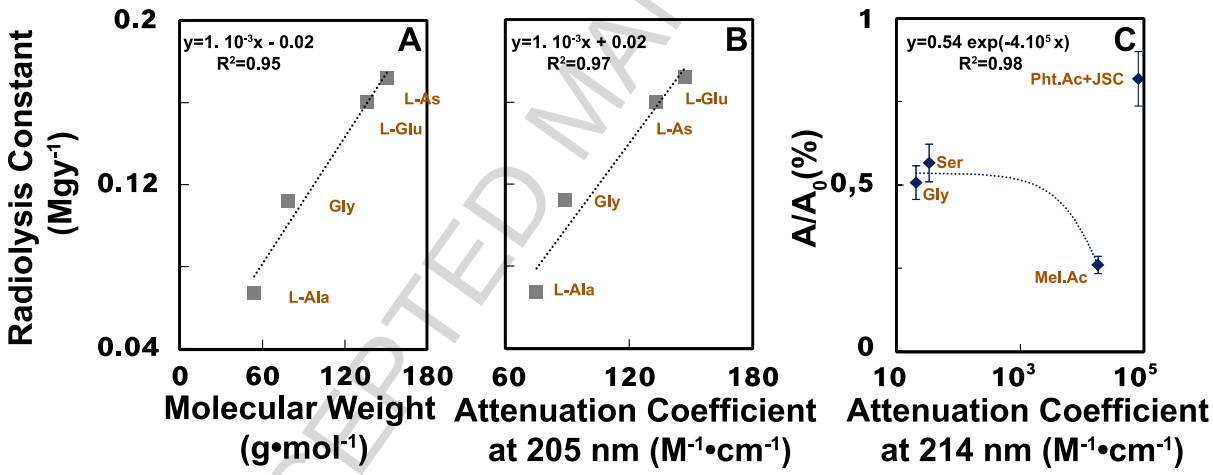

Figure 4. Evolution of the radiolysis constant of amino acids as a function of (A) the molecular weight, and (B) the attenuation coefficient at 205 nm (Radiolysis constant taken from Kminek and Bada 2006, attenuation coefficients from Goldfarb et al. 1951). (C) Relative abundance after irradiation (A/A_0 %) for glycine, melitic acid, and a mixture of phtalic acid and JSC Mars-1 regolith simulant following exposure onboard the International Space Station for 1.5 years (A/A_0 taken from dos Noblet et al. 2012).

3.2 Effect of geological substrate on amino acid survivability

Due to the apparent effect of amino acid shielding by minerals olivine, gypsum, and nontronite, we sought to investigate the potential influence of mineral properties (surface area, pore size), which should be absent for the geological substrates that impart a limited or absent shielding effect (montmorillonite, jarosite, goethite, basaltic lava and saponite). Figure 5A shows amino acid survivability as a function of mineral surface area and pore size determined by dos Santos et al. (2016). In the case of gypsum, olivine and nontronite, which potentially demonstrate a UV shielding effect, survivability decreases with pore size and surface area, as shown by dos Santos et al. (2016).

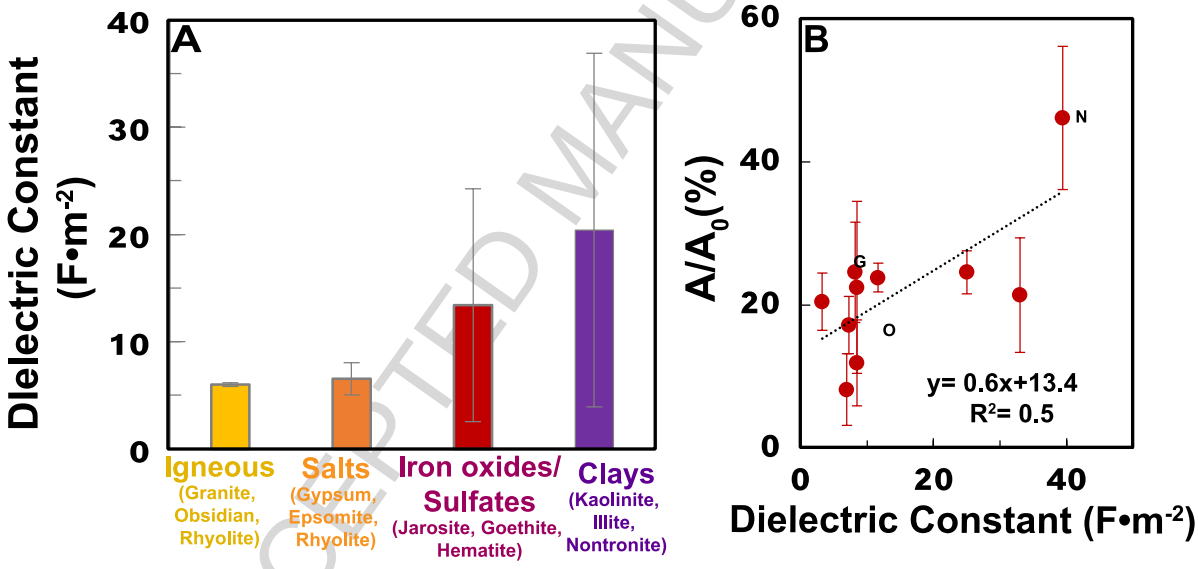

Figure 5. (A) Mean values of the dielectric constant for different classes of rocks of astrobiology interest (indicative values taken data from Olhoeft 1979, Stillman and Olhoeft 2008, and Cunje et al. 2018). (B) Relative abundance of the amino acids after irradiation A/A_0 (%), for amino acids taken from dos Santos et al. (2016), as a function of dielectric constant (reported in table 1). G, N, O stands for gypsum, nontronite and olivine, respectively. Values are the average value for all amino acids per mineral, and error bars are the associated standard deviation (1θ).

The iron content of the mineral/geological substrates investigated shows no protective effect on the survivability of amino acids (Supplementary Figure 1). Conversally, a positive correlation is seen with the dialectric constant and amino acid survivability (Figure 5B).

The dielectric constant is related to the transport of electrical charges within an insulating solid, and is also directly linked to the reflectivity of a solid (Hapke 2012). In solids, the dielectric constant increases with surface area (Knight and Nur 1987), iron content (eg. Krohns et al. 2009; Yang et al. 2012; Chi et al. 2017), and water content (Ling et al. 2016), and decreases with pore size (Kondoh et al, 2001; Palov et al. 2016). Clays have a higher dielectric constant (figure 5A) than iron oxides, salts or igneous rocks. A higher electric constant corresponds to a higher mobility of charge carriers (electrons, electron holes), resulting in reduced charging effects responsible for structural damages in ionised solids (Cazaux 1995). The positive correlation between higher dielectric constant and survivability may indicate that the dielectric constant is a useful top-level parameter for in identifying mineral that are effective at shielding against UV photo-degradatino of organics. In the case of olivine, while it shows here a photo-protective role in the preservation of amino acids, this may be negated by the catalytic behaviour it exhibits with other biomarkers, such as nucleotides (Fornaro et al., 2013, 2018a).

4.3 Effect of Martian climate on the attenuation coefficients of organics

Mars exhibits a variety of different climates, where pressure, temperature and humidity are shown to differ both seasonally and geographically (see Smith 2008 for review). Temperatures as high as 300 K are measured at the Martian equator, while temperatures as low as 200 K are common on Mars during both summer and winter solstices, and not only at the highest latitudes, as shown on Figure 6. Low temperature (considered here below 200 K) has a

positive effect on the preservation of organic biomarkers (Garry et al. 2006, Ten Kate et al. 2006, Nadal et al. 2006), and amino acids like glycine have a destruction rate 5.6 lower between 210 and 294 K when compared to room temperature (Ten Kate et al. 2006). Lower temperature tends generally to lower the exctinction coefficient (e.g. McLachlan et al. 1987), which in turn, increases the overall survivability of amino acids. UV flux at the Martian surface is also controlled by the opacity of the atmosphere due to dust. On Mars, dust storms occur almost exclusively between the spring and autumn equinox (Smith 2008). These dust storms can be global (Cantor 2007), typically for several weeks, and hundrews of localised dust storms may occur each Martian year (Peterfreund 1985). This effect on atmospheric opacity has an important role as dust particles scatter or absorb solar radiation. For example, UV surface flux calculations for the NASA Pathfinder landing site at 77 °S are six times lower on a clear day (opacity $\tau = 0.5$) than during a dust storm ($\tau = 2.0$) (Cockell et al, 2000). This solar attenuation increases at shorter wavelengths and shows significant absorption and scattering in the UV by atmospheric dust, as shown by the τ (opacity), or the single scattering ϖ (the amount of aerosol light attenuation due to scattering) obtained from UV spectrometers on the Phobos 2 spacecraft (Chassefiere et al. 1992) and the Mars Express orbiter (Mateshvili et al. 2007).

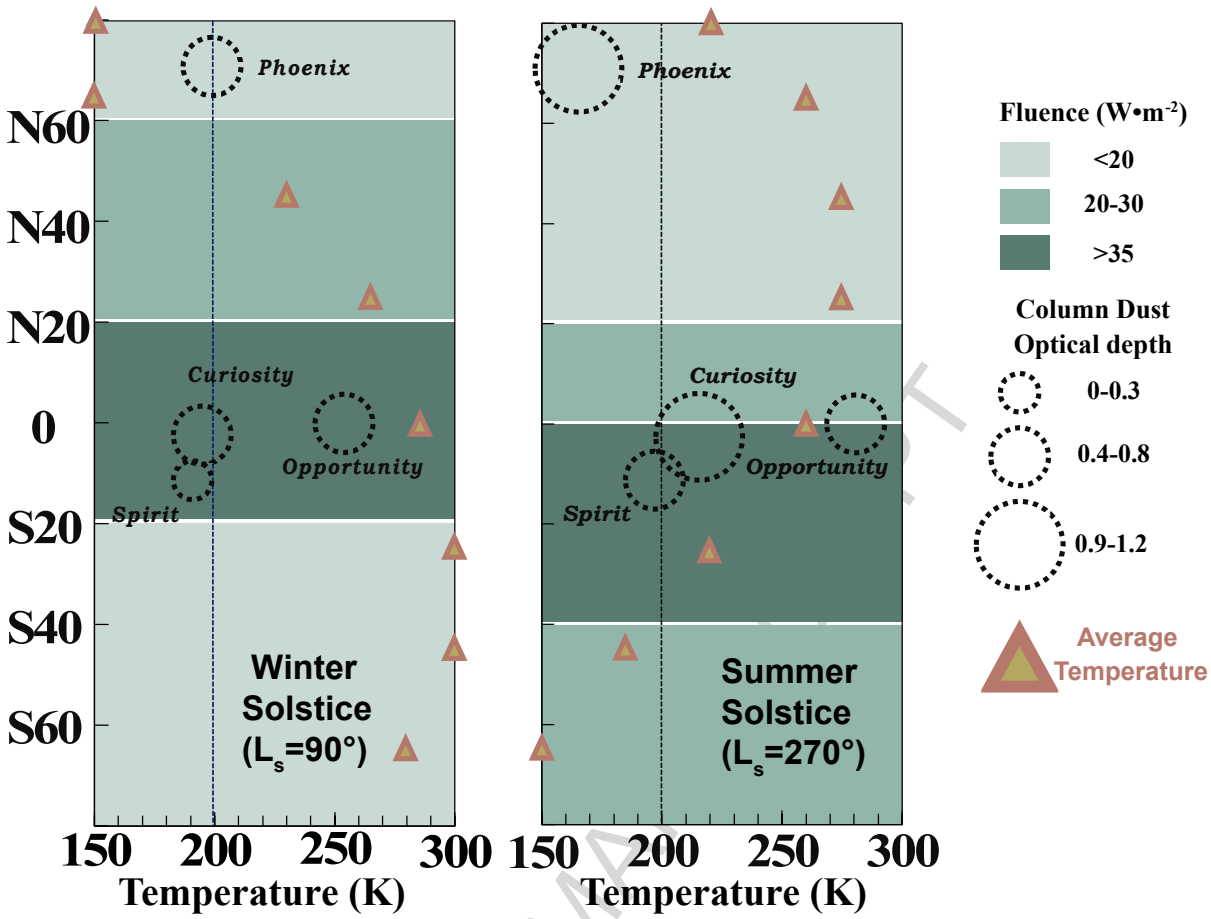

Figure 6. Variability of UV exposure parameters during biannual solstices (L_s=90°, left) and (L_s=270°, right), accounting for surface temperature, opacity (dust column optical depth density) and UV fluence between 200-400 nm, at locations of different landed missions on Mars (Phoenix, Spirit, Curiosity and Opportunity). Data for temperature and opacity are taken for Martian year 26, from the Mars Analysis Correction Data Assimilation (MACDA) Data Collection (Montabone et al. 2011). 200-400 nm UV data are the average value per latitude from Patel et al (2014). Temperature profiles (triangles) are average values per latitude, from Hargitai, 2010.

Therefore, the variation of temperature, atmospheric opacity, and UV activity produce different UV exposure conditions at the Martian surface, even at similar latitudes, on a daily timescale or more. Moreover, the intensity of the parameters potentially neutralize each other, with unexpected outcomes for organic preservation: at low latitude, higher temperatures

increase the destruction rate of organics, but higher temperatures come with higher opacity (Smith 2008), an efficient UV blocker around 200 nm (Chassefiere et al. 1992). At higher latitudes, lower temperatures can help to preserve organics, but with a lower average dust opacity. Nevertheless, the limited dust opacity at high latitude could be balanced by higher ozone column density. Martian ozone is the other atmospheric UV absorber (specially around 255 nm), and modelling indicates that the maximum ozone column densities occur at high latitudes between the autumn and spring equinox (Clancy et al. 2016).

4. Conclusions

In this study, we have highlighted the role of the attenuation coefficient as a control for amino acid survivability, especially when mineral shielding is limited, or absent and confirmed the real shielding effect of gypsum, nontronite, and olivine. These minerals should be explored further as priority targets for the next life- or organic-detection missions, such as Mars 2020 or ExoMars 2020. We also identify that the dielectric constant appears to be a potential parameter in the ability of minerals to shield organics against photo-degradation, as it encompasses many basic physicochemical properties of surface materials (e.g. pore size, or water content). Overall, organic survivability will be directly influenced by the combined factors of the Martian climate, and local surface temperature and atmospheric opacity variations, which can both hinder and mitigate organic survivability. Further experimental works should done in this direction, taking into account opacity, temperature and mid-UV photons, to ensure the maximum chance of detection of organics for the future space missions.

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Highlights

- Attenuation coefficient at 200 nm is an effective parameter for quantifying organic survivability.
- Dielectric constant is a potential key parameter regarding mineral shielding in Martian environment.
- Combination of Martian climatic parameters show a significant latitudinal variation of the relative UV environment.